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TECHNIQUE FOR COLLECTING INTEGRATED SAMPLES OF GASEOUS INDUSTRIAL EFFLUENTS

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TECHNIQUE FOR COLLECTING INTEGRATED SAMPLES OF GASEOUS INDUSTRIAL EFFLUENTS*

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Abstract: A technique for the determination of contaminants in gaseous effluents from both cyclic and continuous industrial operations is presented. The sampling train, made entirely of glass, is easily manipulated in the field to obtain integrated samples over periods up to two hours. Standard mass spectrometric methods of analysis give results to 0.01 mole percent.

Introduction

Under the technical direction of the Public Health Service, the Special Air Pollution Study of Louisville and Jefferson County, Kentucky, is evaluating the contribution to municipal air pollution of numerous industrial plants located southwest of Louisville. In connection with this work, the authors supervised a survey of a synthetic rubber manufacturing plant wherein the problem of sampling gaseous organic emissions was encountered.

The emissions were produced by cyclic and continuous operations and in all cases were discharged to the atmosphere through vents or stacks. To determine the nature and quantity of the contaminants released, it was necessary to have gas sampling equipment for obtaining integrated samples of cyclic operations and normal grab samples of continuous operations. Further, to minimize changes in sample composition after collection, it was considered mandatory that only inert materials be used in the equipment. For practical purposes, this condition eliminated any sampling apparatus not of glass construction.

Since the emissions were to be sampled at their sources, where contaminants would occur in relatively high concentrations, gaseous samples of two liters were considered to be of sufficient size for mass spectrometric analysis. The small sample required for analysis permitted

use of one of the simpler displacement techniques for sampling. The requirement of taking grab samples was easily fulfilled, since much information is available on evacuated or aspirating flask techniques for grab or spot sampling.[1,2,3,4,5] However, existing techniques for continuous sampling employing glass equipment, such as freeze-out or mercury displacement, were too expensive or generally impractical to justify their use in this survey. Therefore, the equipment described in this paper was constructed to satisfy the conditions set forth above.

Equipment

The equipment used in the sampling train (Fig. 1) is made entirely of glass. The sample is collected in a two-liter round-bottom flask sealed by a stopcock in a flask adapter. The adapter joins the sample flask to the sampling manifold. One arm of the manifold is connected to a manometer, and the other arm is attached to the flushing piece and sampling probe during sampling, or to the vacuum connector during initial evacuation of the sample flask. The stopcock, valve A, in the arm of the sampling manifold which connects with the flushing piece is used as the control valve during sampling. Except for the two ground, tapered, flask adapter joints, all components of the system are interconnected by ground ball and socket joints. Rubber vacuum tubing is used to connect the system with a vacuum pump; however, the sampled gas comes in contact with glass only.

When this sampling train is used in the field, the glassware should be mounted rigidly on a framework. In all operations, the investigator should observe normal safety precautions for working with

evacuated equipment, such as taping the flask. Should a larger sample flask be required, it will be realized that the danger of glass failure under high vacuum will be much greater with increased flask size. A low vapor pressure, inert, vacuum grease should be used in the stopcocks, ball and socket joints, and tapered fittings to prevent contamination or absorption of the sample. If the gas stream contains particulate matter, it must be filtered ahead of the control valve to prevent clogging.

Certain of the gaseous components in a stack effluent may be adsorbed on particulate matter present.[6] Selective adsorption properties of filtered solids may introduce an error into the gas analysis. The quantity adsorbed must therefore be determined and applied as a correction factor to the gas analysis if the results warrant such adjustment.

Procedure

Prior to sampling, the apparatus is assembled as in Figure 1 with the vacuum connector installed at point 1. After evacuation of the system to below 1 mm. Hg absolute pressure, valve A is closed and the vacuum connector is replaced by the sampling probe and flushing piece. The probe is then inserted through a small hole in the stack and the probe and flushing piece are purged with stack effluent, using the vacuum pump when necessary. After purging for 2 to 5 minutes, valve B is closed. It has been suggested[7] that in certain cases where extremely accurate results are required or very dilute concentrations are to be measured, the system be treated in the following way prior to sampling: the sampling train is evacuated, filled with the sampled gas, and then re-evacuated before the actual sample is taken. This is done to bring the interior surfaces of the sampling apparatus into equilibrium with the gas and so reduce surface adsorption of any of the sample components.

Sampling is normally started at the beginning of a process cycle, at which time valve A is cracked open and the time noted. As will be pointed out later, the rate of pressure rise in the sampling system is a direct measure of the sampling rate. Hence, sampling rate is controlled by maintaining a constant rate of pressure rise. By repeated observations of this rate of pressure increase, the operator periodically adjusts the control valve to maintain the desired sampling rate. The control of valve A is easily accomplished and, in practice, the sampling period can readily be varied up to two hours.

An approximate method for obtaining an integrated sample may also be used. By this technique the gas is allowed to enter the system in a series of equal increments. The size of the sample increments can be controlled by noting the incremental rise in sampling system pressure during each sampling interval. The control valve is opened just for the time necessary to allow the passage of gas to give the desired rise in pressure and is then closed until the next intake.

Choice of sampling rate will normally depend on the process cycle time. However, this choice may be arbitrary when the process cycle is of such short duration as to require sampling many consecutive cycles or when the discharge is known to fluctuate at random.

Differential pressure across valve A maintains the flow. Since this differential pressure continuously decreases during the sampling period, the opening in the control valve must, after the system reaches the critical pressure ratio, be increased from time to time (see discussion on Sampling Flow Control).

Sampling may be terminated before the sampling system reaches atmospheric pressure. Presence of a slight vacuum will insure sealing of the tapered fittings in the sampling flask during later handling.

Sampling Rate

The rate of absolute pressure increase in the sampling system is a measure of the sampling rate. This can be shown by using the perfect gas law:

$$p = \frac{RT}{MV} m \qquad (1)$$

where
- p = pressure in the sampling system
- m = mass of gas in the sampling system
- R = gas constant
- T = absolute gas temperature in the sampling system
- M = molecular weight of sampled gas
- V = sampling system volume - (i.e., the volume downstream of valve A)

In using equation (1) as the basis for the sampling techniques described previously, it is assumed that the sampling system volume, gas temperature, and molecular weight are constant, since:

1. Sampling system volume increase caused by change in manometer level is negligible.

2. Temperature variation in the contained gas will normally be slight at the low sampling rates used with this equipment. Even with hot stack gases, the gas temperature at valve A approximates ambient conditions because of free dissipation of heat during passage through

the sampling probe. In extreme cases, it may be necessary to extend the probe or to cool it externally in order to bring the sampled gas temperature down to that of the environment.

3. Molecular weight change will be negligible for minor variations in gas composition. If, however, the gas composition varies during the sampling period in such a way as to markedly affect the molecular weight, there will exist an error in sampling rate proportional to the change in molecular weight.

Expressing equation (1) in the differential form where T, M and V are assumed constant:

$$dp = \frac{RT}{MV}\, dm \qquad (2)$$

Integrating between p_1 and p_2 with the corresponding limits of m_1 and m_2,

$$\int_{p_1}^{p_2} dp = \frac{RT}{MV} \int_{m_1}^{m_2} dm \qquad (3)$$

$$p_2 - p_1 = \frac{RT}{MV} (m_2 - m_1) \qquad (4)$$

Therefore, equal increments of pressure yield equal increments of weight of gas sampled independent of the absolute pressure in the sampling system.

Further, differentiating equation (1) with respect to time:

$$\frac{dp}{dt} = \frac{RT}{MV}\frac{dm}{dt} \qquad (5)$$

Since during sampling $\frac{dp}{dt}$ is held constant, then $\frac{dm}{dt}$ is also constant. Therefore, as long as the rate of pressure rise is held constant, the sampling rate will be constant.

Sampling Flow Control

In designing this sampling train, it was necessary to select a mechanism suitable for sampling rate control. The Naval Medical Research Institute [8] has used a sampling train in which a critical or sonic orifice gives constant flow into a 16-liter steel sample flask. There are, however, certain inherent limitations in a critical flow device for stack gas sampling; namely, (1) a separate orifice is required for each sampling rate desired, (2) the possibility of plugging exists when extremely small orifices are used, and (3) sampling can be continued at constant rate only until critical flow ceases, at which time, for air, the sampling system pressure is approximately 0.53 times the upstream pressure.[9]

In preliminary tests it was found that, in a two-liter sample, an orifice to maintain critical flow for at least thirty minutes was so small that moisture, dust, etc., repeatedly plugged the aperture. For this reason, another means was sought for maintaining constant flow, even though for samples of larger volume or for shorter sampling times, a sonic orifice might be practicable.

Manually operated valves were considered for application in the sampling train. A glass stopcock was found to offer sufficiently fine sampling rate control and was incorporated into the system. It can be seen that a partially opened stopcock forms two segmental orifices within its housing. From a mathematical treatment of flow through any two orifices in series, it can be shown that for a stopcock, wherein the upstream and downstream segmental orifice areas are about equal, the flow can be sonic only at the downstream orifice. Further, if the sampled gas approximates air at one atmosphere pressure, critical flow will cease when the flask pressure reaches 0.39 atmospheres. That is, 0.39 represents an effective critical pressure ratio for the case where two equal orifices are in series. Beyond this point, which is substantially lower than the critical pressure ratio for a system containing one orifice, the selected flow rate must be maintained by periodic adjustments of the stopcock.

Sample Analysis

Gaseous samples may be analyzed by mass spectrometry. In most cases, a portion of the sample is pumped from the flask directly to the analysis cell and a spectrum obtained. From this spectrum, the partial pressure and hence the mole percent of each compound present are determined.

Where samples contain only trace amounts (< 0.1 mole percent) of some compounds, a more refined analytical technique is required. A procedure used by the National Bureau of Standards [10] is outlined below. Here the trace compounds are concentrated by condensation at liquid

nitrogen temperature (-320°F.). The noncondensables are then pumped off and the sampling flask is allowed to warm to room temperature. The condensed fraction, now in the gaseous state, is then analyzed as before and the new concentrations are related to the original sample by comparison of the respective CO_2 concentrations. An alternate method of relating trace compounds to the original sample involves measuring the flask pressure before and after condensation. The fractional change in flask pressure is equivalent to the total partial pressures of the condensable materials in the original sample. From this information and the analysis of the condensables, the concentration of the trace compounds in the original sample is calculated.

In a two-liter sample, the minimum concentration that can be measured is of the order of 0.01 mole percent. Larger samples will, of course, extend the limit of detection proportionately. As with any sampling technique, the sample must not change in composition by surface adsorption or reaction during the time between collection and analysis. If the gas to be sampled contains highly reactive components, such as some acid gases, it is suggested [4] that other methods which eliminate prolonged storage of the sample be used for sampling and analysis.

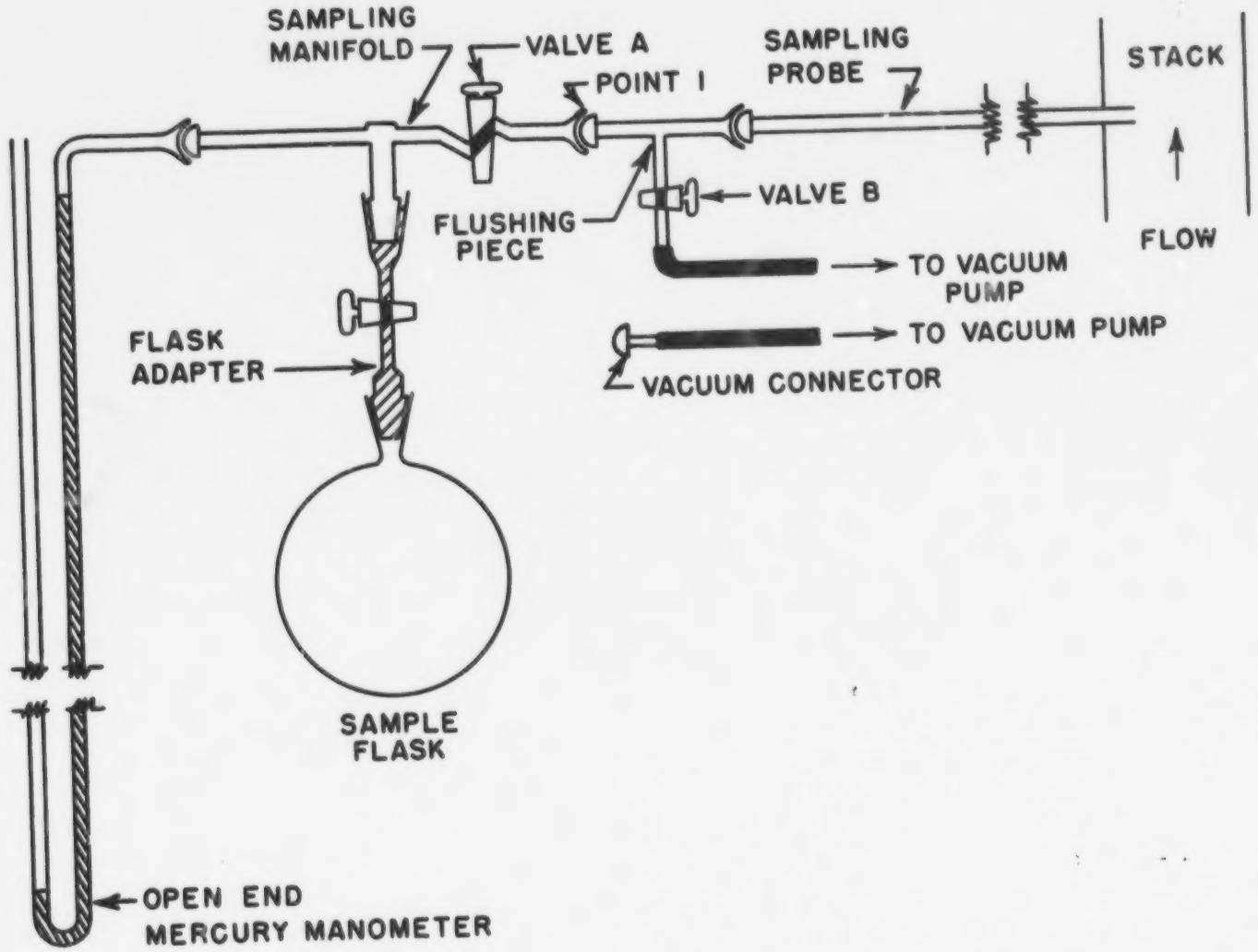
Field Application

The sampling and analytical techniques described herein were used satisfactorily in the synthetic rubber plant survey mentioned. The contaminant effluent rates were calculated from analytical data obtained from 27 flask samples, including duplicates, collected at representative

points. Samples were analyzed by the Mass Spectrometry Section, National Bureau of Standards, U. S. Department of Commerce in Washington, D. C.

The sampling data gave contaminant concentrations ranging from 0.03 to 70.2 mole percent. From these data, the total organic emission from the plant was found to be of the order of 10 tons per day. Careful material-balance estimates of these emissions, independently prepared by plant personnel, agreed with these values within six percent. The company's inventory loss estimates were made on the basis of total plant consumption, and hence, comparison for individual stacks was not possible.

In summary, a method has been developed for collecting gaseous samples of effluents from both cyclic and continuous industrial operations. The equipment is simple and easily operated to give samples which can be analyzed by mass spectrometry. Field use of this method has indicated that it may be easily adapted to other similar applications.



APPARATUS USED FOR OBTAINING INTEGRATED SAMPLES OF GASEOUS INDUSTRIAL EFFLUENTS

FIGURE 1

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